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Evaluation of Silica Gel Cartridges Coated In situ with Acidified 2,4-Dinitrophenylhydrazine for Sampling Aldehydes and Ketones in Air

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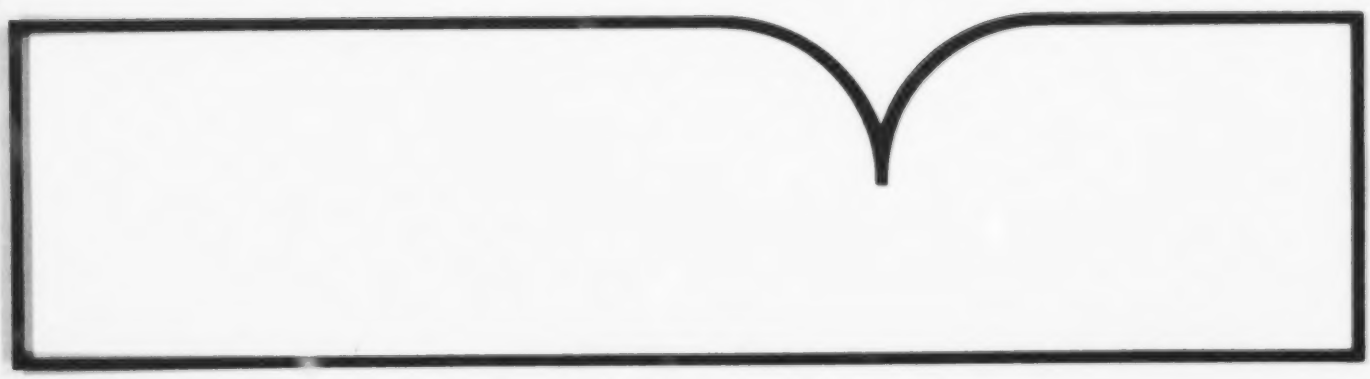

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16. ABSTRACT

A procedure for coating in-[illegible]silica in commercially available prepacked cartridges with 2,4-dinitrophenylhyd[illegible](DNPH) acidified with hydrochloric acid is described. The coated cartri[illegible] compared with a validated DNPH impinger method for sampling organic carbonyl co[illegible]ds (aldehydes and ketones) in diluted automotive exhaust emissions and in ambient air for subsequent analysis of the DNPH derivatives by high performance liquid chromatography. Qualitative and quantitative results show that the two sampling devices are equivalent. The cartridge device is superior to the impinger in terms of analytical sensitivity and convenience, especially for field applications.

An unknown degradation product of acrolein has been tentatively identified as x-acrolein. The disappearance of acrolein in the analytical sample matrix correlated quantitatively almost on a mole for mole basis with the growth of x-acrolein. The sum of the concentration of acrolein and x-acrolein appears to be invariant with time. This sum could possibly be used as a more accurate value of the concentration of acrolein in the integratated sample.

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Evaluation of Silica Gel Cartridges Coated *In Situ* with Acidified 2,4-Dinitrophenylhydrazine for Sampling Aldehydes and Ketones in Air

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(*Received February 3, 1986*)

A procedure for coating *in situ* silica gel in prepacked cartridges with 2,4-dinitrophenylhydrazine (DNPH) acidified with hydrochloric acid is described. The coated cartridge was compared with a validated DNPH impinger method for sampling organic carbonyl compounds (aldehydes and ketones) in diluted automotive exhaust emissions and in ambient air for subsequent analysis of the DNPH derivatives by high performance liquid chromatography. Qualitative and quantitative data are presented that show that the two sampling devices are equivalent. The coated cartridge is ideal for long-term sampling of carbonyls at sub to low parts-per-billion level in ambient air or for short-term sampling of carbonyls at low ppb to parts-per-million level in diluted automotive exhaust emissions.

An unknown degradation product of acrolein has been tentatively identified as *x*-acrolein. The disappearance of acrolein in the analytical sample matrix correlates quantitatively almost on a mole for mole basis with the growth of *x*-acrolein. The sum of the concentration of acrolein and *x*-acrolein appears to be invariant with time.

KEY WORDS: Sampling cartridge, HPLC analysis, formaldehyde, carbonyl compounds, 2,4-dinitrophenylhydrazine.

INTRODUCTION

Aldehydes and hydrocarbons have been shown in the laboratory to play critical roles in the chemistry of polluted air. Formaldehyde, for example, when irradiated in a dilute mixture of NO_2 in air,[1] promotes the formation of photochemical ozone. Even in the absence of NO_x, aliphatic aldehydes have been observed to induce photochemical oxidation of olefinic and aromatic hydrocarbons when exposed to ultraviolet light.[2] Short-term exposures to specific aldehydes (formaldehyde, acetaldehyde, acrolein, crotonaldehyde) are known to cause irritation of the eyes, skin, and mucous membrane of the upper respiratory tract.[3]

Very limited speciated aldehyde data in source emissions and in ambient air are available in the literature despite the great need for these data in air quality assessment and health-related studies. Most of the published data is limited to formaldehyde. One main reason for this deficiency is the absence, until recently, of a sensitive, specific, and convenient analytical method of measuring aldehydes.

Several papers were published in the last six years dealing with sampling and analysis of aldehydes, principally formaldehyde, in air.[4–30] The most specific and sensitive analytical method widely used to date is based on the reaction of organic carbonyls (aldehydes and ketones) with 2,4-dinitrophenylhydrazine (DNPH) and subsequent analysis of the hydrazone derivatives by high performance liquid chromatography (HPLC).

A DNPH/acetonitrile (ACN) impinger technique was first reported by Kuntz *et al.*[8] and by Lipari and Swarin[15] and was validated for measurements of carbonyls in ambient air and in mobile source emissions. In contrast to other impinger methods using different solvents for the DNPH absorbing solution, the DNPH/ACN technique permitted direct analysis of the absorbing solution by reversed-phase HPLC with very minimal sample preparation. With minor modifications, this improved sampling technique was used to measure carbonyls in mobile source emissions,[31] in ambient atmospheres near an urban roadway,[32] and in indoor atmospheres of residential homes.[33] The method was also used to measure seasonal variations of formaldehyde and acetaldehyde in ambient atmospheres[25] and carbonyl emissions from woodburning fireplaces.[29]

The DNPH/ACN impinger technique has greatly simplified the

sampling of carbonyls. However, it is still cumbersome for field use especially when samples have to be stored and transported to a central laboratory for analysis. Moreover, because of solvent evaporation, the technique is not ideally suited for sampling carbonyls at sub and low parts-per-billion (ppb) level in which an extended sampling time and/or high flow rates are needed to obtain adequate sample enrichment for HPLC analysis without additional sample preparation.

The use of solid traps remedies some of the shortcomings of the impinger technique. A number of cartridge devices containing solid sorbents coated with DNPH have recently been used with varying success for sampling aldehydes in air. The solid sorbents include XAD-2,[5,12] silica gel,[7,23] glass beads,[13] octadecylsilane-bonded silica gel,[21] Florisil,[29] and glass fiber filters.[30] Some of these collection devices require tedious preparation[5,7,13] and long elution time,[5,7,13] as well as additional sample handling of the eluate prior to HPLC analysis.[30]

Kuwata *et al.*[21] coated octadecylsilane bonded silica gel in prepacked plastic cartridges (Sep-PAK C_{18}) with DNPH acidified with 1% phosphoric acid. The device was used for sampling carbonyls in three different ambient environments. Their data looked impressive, unfortunately, no validation of the cartridge sampling technique against an independent sampling method, e.g. DNPH/ACN, was conducted. Questions about the possibility of interference and sampling artifacts were not adequately addressed.

Lipari and Swarin[29] reported efficient collection of formaldehyde in ambient air and diluted automotive exhaust emissions with prepacked Florisil (Thermosorb/F) cartridges coated with DNPH without any acid. Excellent agreement between the cartridge and the DNPH/ACN sampling methods was obtained for formaldehyde. No comparative results, however, were presented for the other carbonyl compounds, e.g. acetaldehyde, acrolein, acetone, etc., that are known to be present in these sample types.

We observed during our exploratory attempts to duplicate the method of Kuwata *et al.*[21] with the Sep-PAK C_{18}, that the acetone background of the coated blank cartridge was significantly greater than the amount of acetone originally present in the volume of coating solution charged into the cartridge. Furthermore, in contrast to reference 21, carbonyl compounds with molecular weights greater

than hexanaldehyde were also observed. The concentration of these carbonyls increased with length of storage of the coated cartridge. Similar type high molecular weight carbonyl backgrounds were also observed with silanized glass wool that was coated with acidified DNPH. The magnitude of this carbonyl background showed dependence on the concentration and type of mineral acid used in the DNPH coating solution, i.e. $H_3PO_4 < HCl < HClO_4$. These carbonyls could have resulted from the acid mediated breakdown of the chemisorbed organic coatings on silica gel.

As a consequence of these initial observations, we chose to evaluate silica gel Sep-PAK as a sorbent substrate for acidified DNPH and also opted for HCl rather than H_3PO_4 as the acid catalyst.

This paper presents the results of our evaluation of the suitability of silica gel Sep-PAK coated with acidified DNPH for sampling carbonyls in air. The cartridge coating method we described is simpler than most procedures in the literature and is suitable for mass production of DNPH-coated cartridges with consistently low carbonyl background. Supportive qualitative and quantitative data showing the equivalence of this cartridge device and the validated DNPH/ACN impinger method for sampling carbonyls in air are provided. The separation and initial identification of the probable transformation product of acrolein hydrazone is reported for the first time.

EXPERIMENTAL SECTION

Reagents and chemicals

All organic solvents were "distilled-in-glass" HPLC grade solvents (Burdick & Jackson Laboratories, Muskegon, MI).

DNPH (Aldrich Chemical Co., Milwaukee, WI) was purified by multiple recrystallization in HPLC grade ACN. Recrystallization was accomplished at 40–60°C by slow evaporation of the solvent to maximize crystal size. Large crystals facilitated the removal of surface impurities and minimized the loss of the purified material during rinsing. Final removal of impurities was performed with a special glass apparatus which was also used for storing the purified crystals. The apparatus is basically a glass tubing (4 cm I.D. × 15 cm

long) fitted with a high porosity glass filter frit and a three-way stopcock at one end and a standard stoppered connection at the other end. A glass stopper, with a vented connection to a DNPH-coated silica cartridge, minimized exposure of the purified material to carbonyl-contaminated laboratory air. About 50 mL of ACN was maintained above the purified crystals at all times as the source of saturated DNPH stock solution for various analytical applications. Impurity level of the stock solution was checked by HPLC analysis. The concentration of the stock solution was about 11 mg DNPH/mL at room temperature.

The impinger absorbing solution was prepared by diluting 10 mL of saturated DNPH stock solution to 200 mL with ACN and adding 2 mL of 3.8 M perchloric acid. Twenty milliliters of the absorbing solution were used for each impinger. Formaldehyde, acetaldehyde and acetone were usually observed in the blank absorbing solutions at concentrations typically less than 0.01 ug/mL measured as hydrazones.

The hydrazone derivatives used as gravimetric standards were prepared by reaction of individual carbonyl compounds with saturated DNPH solution in 2 N HCl. Purity was determined by melting point measurement and HPLC analysis. Calibration standards were prepared by dissolving known quantities of the hydrazone derivatives in ACN.

Preparation of DNPH-coated silica cartridges

Prepacked silica cartridges (Sep-PAK), purchased from Waters Associates (Milford, MA) contain about 0.7 g of silica gel (approximately 100 mesh) compactly sealed in a plastic tube (1 cm o.d. × 2 cm long) by inert plastic filter frits. The cartridge body terminates at both ends as small tubes that can be conveniently connected to a standard male Luer syringe port.

The cartridge was washed by gravity feed elution of 10 mL of ACN from a plastic syringe reservoir. The ACN wash was immediately followed by gravity feed elution of 7 mL of acidified DNPH-coating solution. The DNPH-coating solution was prepared by diluting 25 mL of the saturated DNPH stock solution to 1 L with ACN and adding 1 mL of concentrated HCl. Excess solvent was removed by blowing aldehyde-free nitrogen (passed through a

DNPH-coated cartiridge) at 0.3–0.4 L/min for 15 min. The cartridge was stored in the refrigerator in an all-glass, capped container. The cartridge contains about 1.9 mg of DNPH. Coated cartridges were usually mass produced in lots of 50 to 100. To produce a consistent lot, positive displacement repetitive pipet dispensers were used for mass cleaning and coating of the cartridges.

Typical concentrations of impurities as hydrazones when a cartridge was eluted with 5 mL ACN ranged from 0.02–0.07 ug/mL, 0.01–0.02 ug/mL, and 0.02–0.06 ug/mL for formaldehyde, acetaldehyde and acetone respectively.

Instrumentation

A Varian model 5000 gradient liquid chromatograph equipped with an automatic sampler and a 25 uL sample loop was used. Detection at 360 nm was obtained with an ISCO model 1840 variable wavelength detector. HPLC separation was accomplished on two DuPont Zorbax ODS columns (4.6 mm by 25 cm) connected in series, using a gradient program from 60% to 100% ACN in water at 1 mL/min. Quantitation by peak area integration was obtained with a Spectra Physics computing integrator.

Sampling

Automotive emissions sampling was conducted on a constant volume sampler (CVS) dilution tunnel with vehicles operating on a prescribed driving schedule on a chassis dynamometer. Sample lines and probe were heated to about 100°C to prevent condensation. Impinger samples were collected nominally at 1 L/min, and parallel cartridge samples were collected via a four-port heated glass manifold at 0.25 to 1.0 L/min. The cartridges were used either singly or two in series. Short pieces of Teflon FEP tubing that were heat flared at both ends were used to connect the cartridges. Flow was controlled either with needle valves or mass flow controllers (Tylan Corp., Carson, CA) and monitored using a Hasting mass flow meter (Teledyne Hasting-Raydist, Hampton, VA). All samples were collected using model MB-21 metal bellows pumps (Metal Bellows Corp., Sharon, MA) for the impinger and each of the cartridges.

Ambient air samples were collected using a pumping system

similar to the one used in exhaust emissions sampling. The cartridges were used as direct probes and traps for sampling ambient air when the temperature was above freezing, and heated glass probe and manifold was used when ambient temperature was below freezing. Typical flow rate through one cartridge was about 1.5 L/min and about 0.8 L/min for two cartridges in series. Impinger samples were collected, depending on sampling duration, at 0.5–2.0 L/min through a heated glass probe. Generally two impingers in series, each containing 20 mL of acidified DNPH solution were used. When parallel impinger and cartridge samples were collected, outputs of each of the sampling pumps were sequentially directed to a calibrated mass flow meter for a 10 min duration. Flow for each sequence was monitored with an analog recorder.

Each of the impinger samples was quantitatively transferred to a 25 mL volumetric flask and brought to volume with ACN. The cartridge samples were eluted in reversed direction by gravity feed with 6 mL of ACN. The eluate was collected in a graduated test tube and made up to the 5 mL mark with ACN. Both the impinger and cartridge samples were analyzed by HPLC without additional sample preparation.

Compound identification

The carbonyl compounds were identified by comparison of their retention times with those of standard samples. In order to get reasonable estimates of total carbonyl content, unknown peaks between propionaldehyde and crotonaldehyde, were assigned the response factor and molecular weight of propionaldehyde and were collectively called *x*-propionaldehyde. An important exception is an unknown peak which we have labelled *x*-acrolein and is assigned the response factor and molecular weight of acrolein. In the same manner unknown peaks between crotonaldehyde and benzaldehyde were collectively called *x*-butyraldehyde; peaks between benzaldehyde and *o*-tolualdehydes, were collectively called *x*-valeraldehyde. Unknown peaks adjacent to 2,5-dimethylbenzaldehyde were collectively called *x*-2,5-dimethylbenzaldehyde. Other minor components that elute much later than 2,5-dimethylbenzaldehyde were not assigned response factors for lack of appropriate standards.

RESULTS AND DISCUSSION

The DNPH-coated silica cartridge was compared with a validated DNPH/ACN method for sampling carbonyls in diluted automotive exhaust emissions and in ambient air. Three vehicles, each operating with a different fuel (a 90% methanol, 10% gasoline blend; gasoline; and diesel), were used. Ambient air samples were collected from a chemical laboratory, a parking lot, and a residential area with a high concentration of woodburning fireplaces. Samples were collected simultaneously with one or two impingers in series and one to three parallel cartridges. Some samples were collected with two cartridges in series.

Since the DNPH/ACN method has already been validated by several investigators for sampling carbonyl compounds in dilute automotive exhaust emissions and in ambient air,[8,15,27] it is taken to be the reference method in the evaluation of the cartridge technique. The evaluation proceeded in two steps: (1) a qualitative comparison was made of the HPLC carbonyl profiles of air samples simultaneously collected with the cartridge and impinger devices and (2) a quantitative comparison of individual carbonyl species in both samples was determined.

Figure 1 shows some typical comparative profiles of carbonyl emissions from the three vehicles. Formaldehyde is by far the most abundant carbonyl emitted. The general features of the profiles of corresponding cartridge and impinger samples are very similar, with the exception of the C_3 and C_4 carbonyl regions. Acrolein, relative to acetone and propionaldehyde, is higher in the impinger than in the cartridge samples. This is clearly illustrated in the case of exhaust emissions from gasoline- and diesel-fueled vehicles. An unknown peak, eluting immediately after propionaldehyde, was observed to be present at a higher level than acrolein in the cartridge than in the corresponding impinger samples. This peak was not present initially in the impinger sample of exhaust emissions from a gasoline vehicle but was observed to grow with time. When this peak was assigned the response factor and molecular weight of acrolein, its growth in the impinger sample was found to correlate almost on a mole for mole basis with the disappearance of acrolein. The sum of the concentration of this unknown species and acrolein in the impinger sample appears to be invariant with time as shown in Table I.

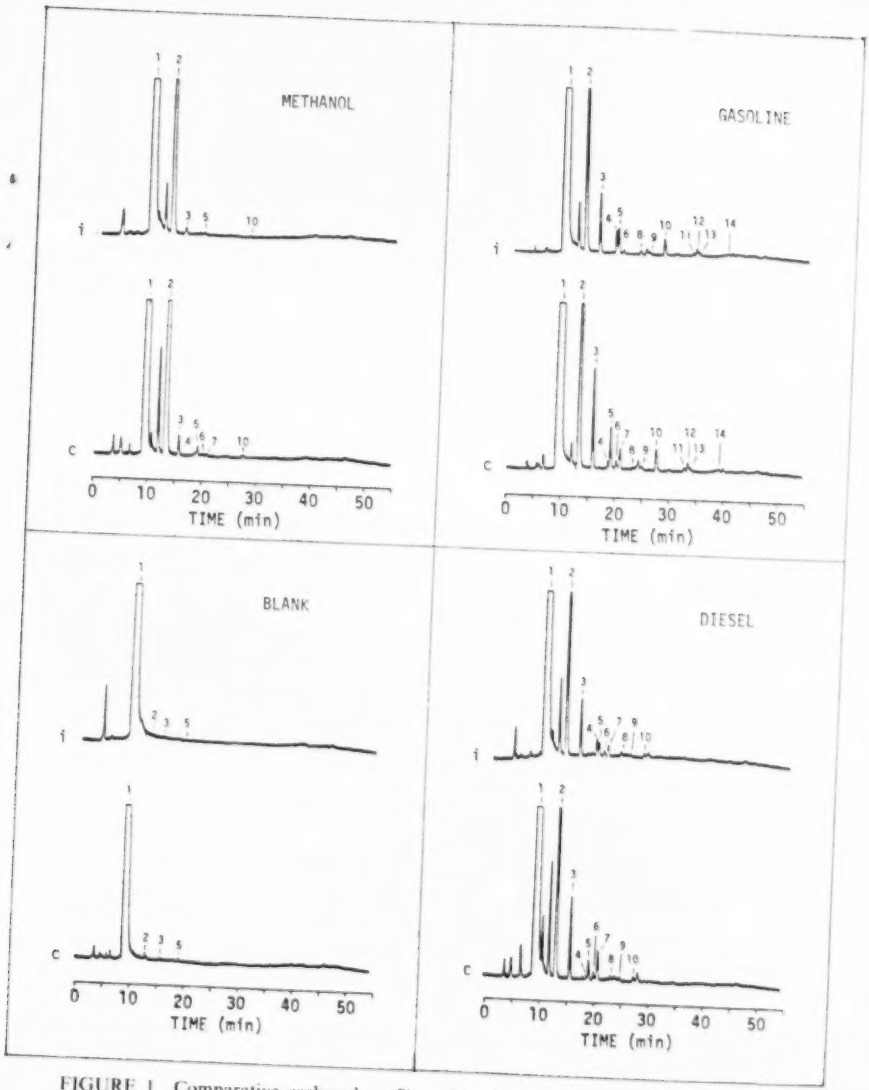

FIGURE 1 Comparative carbonyl profiles of impinger (*i*) and DNPH-coated cartridge (*c*) samples. Samples are diluted exhaust emissions from three different vehicles, each using a different fuel as shown. Conditions: Column, 2 Zorbax ODS (4.6 × 250 mm) in-series; mobile phase, ACN water at 1 mL min; sample volume, 25 μL; detection wavelength, 360 nm; program, on sample injection, linear gradient from 60% to 75% ACN in 30 min, linear gradient from 75% to 100% ACN in 20 min, hold at 100% ACN for 5 min, reverse gradient to 60% in 1 min, equilibriation at 60% for 15 min. Peak identities: 1, DNPH; 2, formaldehyde; 3, acetaldehyde; 4, acrolein; 5, acetone; 6, propionaldehyde; 7, *x*-acrolein; 8, crotonaldehyde; 9, butyraldehyde; 10, benzaldehyde; 11, *o*-tolualdehyde; 12, *m*-tolualdehyde; 13, *p*-tolualdehyde; 14, 2,5-dimethylbenzaldehyde.

TABLE I

Invariance of the sum of concentrations of acrolein and x-acrolein observed in an impinger sample of exhaust emissions from a gasoline fueled vehicle.

	Concentration in ppb		
Time (hr)	Acrolein	x-Acrolein	Sum
0	58.5	0	58.5
25	46.6	11.7	58.3
35	42.2	12.9	55.1

Although these data are very limited, they lend support to our initial conclusion that this unknown species must be a degradation product of acrolein. We accordingly labelled it as *x*-acrolein. To our knowledge, this is the first reported HPLC separation of this species and the first time a growing peak was linked to the disappearance of acrolein hydrazone in the sample matrix. There are indications that crotonaldehyde may degrade in a similar manner. Like acrolein, crotonaldehyde is an olefinic aldehyde. Its abundance in the samples, however, was only about one sixth to one tenth that of acrolein. A clearcut identification of the corresponding *x*-crotonaldehyde was not possible.

Quantitative agreement between the cartridge and the impinger for automotive emissions sampling is generally very good, as typified by results given in Table II. Comparing normalized concentrations of individual carbonyls relative to formaldehyde is another way of comparing both sampling techniques. This factors out sample size in the comparison and most of the experimental errors resulting from small variations in flow. Moreover, it is also helpful in flagging carbonyl species that may degrade in the sample matrix or may be formed as sampling artifacts. For stable species, corresponding normalized concentrations should be about equal for samples collected by both techniques. This holds true for formaldehyde, acetaldehyde, acetone, propionaldehyde, benzaldehydes, and the tolualdehydes but not for acrolein and *x*-acrolein.

The major disagreement between the cartridge and the impinger results is acrolein. The impinger values are much higher than the

TABLE II

Typical comparative results of cartridge and impinger sampling of diluted exhaust emissions from a gasoline-powered vehicle.

	Concentration			
	(ppb)		(Normalized)	
	Impinger	Cartridge	Impinger	Cartridge
Formaldehyde	1109.05	1092.31	1.0000	1.0000
Acetaldehyde	144.33	130.96	0.1301	0.1199
Acrolein	39.96	19.18	0.0360	0.0176
Acetone	82.32	73.40	0.0742	0.0672
Propionaldehyde	6.70	7.75	0.0060	0.0071
Crotonaldehyde	3.43	2.56	0.0031	0.0023
Butyraldehyde		8.06		0.0074
Benzaldehyde	32.33	28.65	0.0292	0.0262
o-Tolualdehyde	4.83	5.23	0.0044	0.0048
m-Tolualdehyde	15.71	12.46	0.0142	0.0114
p-Tolualdehyde	4.31	3.48	0.0039	0.0032
x-Butyraldehyde	19.21	24.70	0.0173	0.0226
x-Acrolein	6.12	24.03	0.0055	0.0220
Acrolein + *x*-Acrolein	46.08	43.21	0.0415	0.0396
Sampling flow, L/min	0.96	0.28		
Sampling time, min	12.75	12.75		

cartridge values. Acrolein values in duplicate cartridge samples do not even agree. However, when the concentration of acrolein is added to that of *x*-acrolein, the agreement of the sum is excellent between the cartridge and the impinger. This result suggests that both devices have equivalent collection efficiencies for acrolein. The observed discrepancy in the acrolein values in the impinger and cartridge samples is due to an apparently large difference in the rates of conversion of acrolein in the matrix. The invariance with time of the sum of concentration of acrolein and *x*-acrolein, noted earlier with the gasoline impinger sample, suggests that this sum for both the impinger and cartridge samples can be used to estimate an accurate integrated concentration of acrolein.

The equivalence of the cartridge and impinger devices is further supported by a recent analysis of solutions of parallel impinger and

cartridge samples of exhaust emissions that have been stored in the refrigerator for eight months. Both samples exhibited almost identical profiles with all acrolein converted to *x*-acrolein.

Table III summarizes the results of comparison of cartridge and impinger techniques for sampling automotive exhaust emissions. Stable carbonyls (formaldehyde, acetaldehyde, acetone, propionaldehyde, and the tolualdehydes) have mean cartridge-to-impinger ratios of about 1.00 and an RSD range of about 4–30% for the gasoline vehicle. The high scatter is associated with carbonyls present at low ppb levels. Acrolein has the lowest (0.38) and *x*-acrolein the highest (3.47) mean ratio. Scatter for these two species, at 48 and 68% RSD respectively, is also high. The mean ratio (0.92) of the sum is more in line with those of the stable species and the scatter, 14.7% RSD, falls within range as well. Crotonaldehyde is the only other carbonyl compound that showed cartridge-to-impinger ratio significantly far from unity.

Acrolein, again, has the lowest mean cartridge-to-impinger ratio (0.35) and the highest scatter (53.3% RSD) among the major carbonyls in diesel exhaust emissions. The mean ratios are practically the same as those in the gasoline exhaust emissions. The propionaldehyde mean ratio (3.52) appears to be abnormally high; however, there was significant contribution from *x*-acrolein as this species was not resolved initially from propionaldehyde under the chromatographic conditions used. An excellent correlation is obtained when the corresponding sums of acrolein and propionaldehyde are compared.

Very good correlations were obtained between cartridge and impinger mean ratios for formaldehyde (1.04) and acetaldehyde (1.08) in exhaust emissions from the methanol-fueled vehicle. Percent RSD is within 10% for both species. Data for the other carbonyls show high scatter principally due to low concentrations of the species.

Figure 2 shows carbonyl profiles of an ambient air sample from a residential site with a high concentration of woodburning fireplaces. Both the impinger and cartridge samples were collected for 12 h. Sampling rate through the impinger was limited to about 0.5 L/min due to solvent evaporation. Although the distribution of the major carbonyls in both samples is about the same, the profiles clearly illustrate that a much higher degree of analytical sensitivity can be achieved with the cartridge than with impinger sampling. As a

TABLE III

Summary comparison of cartridge and impinger for sampling carbonyl compounds in diluted automotive exhaust emissions.

	Cart/Imp Ratio	Sigma	n	Conc. range (ppb) Low	High	RSD
Gasoline vehicle						
Formaldehyde	1.00	0.04	6	247	1256	3.7
Acetaldehyde	0.97	0.06	6	30	178	6.7
Acrolein	0.38	0.18	5	7	69	48.0
Acetone	1.00	0.10	6	37	87	9.7
Propionaldehyde	1.02	0.20	5	7	25	19.2
Crotonaldehyde	0.49	0.19	4	2	14	38.2
Benzaldehyde	0.98	0.08	5	26	65	7.7
o-Tolualdehyde	0.98	0.15	2	4	12	15.1
m-Tolualdehyde	1.08	0.30	5	9	31	27.7
p-Tolualdehyde	0.99	0.19	4	3	8	18.9
x-Butyraldehyde	1.27	0.30	5	9	36	23.3
x-Acrolein	3.47	2.19	4	4	32	63.3
Acrolein + *x*-Acrolein	0.92	0.14	6	2	44	14.7
Sample volumes: Impinger = 8–14 L; Cartridge = 2.4–3.9 L						
Diesel vehicle						
Formaldehyde	1.03	0.07	6	389	619	7.0
Acetaldehyde	1.02	0.11	6	96	139	10.5
Acrolein	0.35	0.19	5	9	77	53.3
Acetone	0.91	0.11	6	25	45	12.4
Propionaldehyde	3.52	1.01	6	15	97	28.7
Crotonaldehyde	1.05	0.14	6	14	23	13.0
Butyraldehyde	1.49	0.18	6	9	17	11.8
Benzaldehyde	1.28	0.22	6	15	26	17.3
Acr + Prop†	1.00	0.03	6	67	101	3.5
Sample volumes: Impinger = 8–14 L; Cartridge = 2.4–7.6 L						
Methanol vehicle						
Formaldehyde	1.04	0.09	9	303	2454	8.5
Acetaldehyde	1.08	0.08	7	11	21	4.4
Acrolein	1.29	0.54	5	1	6	42.3
Acetone	0.76	0.41	7	2	10	54.4
Propionaldehyde	0.28	0.02	3	1	3	6.4
Acr + *x*-Acr	1.20	0.51	5	1	6	43.0
Acr + *x*-Acr + Prop†	0.73	0.30	5	2	7	41.4
Sample volumes: Impinger = 8–14 L; Cartridge = 4.8–13.4 L						

†Acr is acrolein, *x*-Acr is *x*-acrolein, Prop is propionaldehyde.

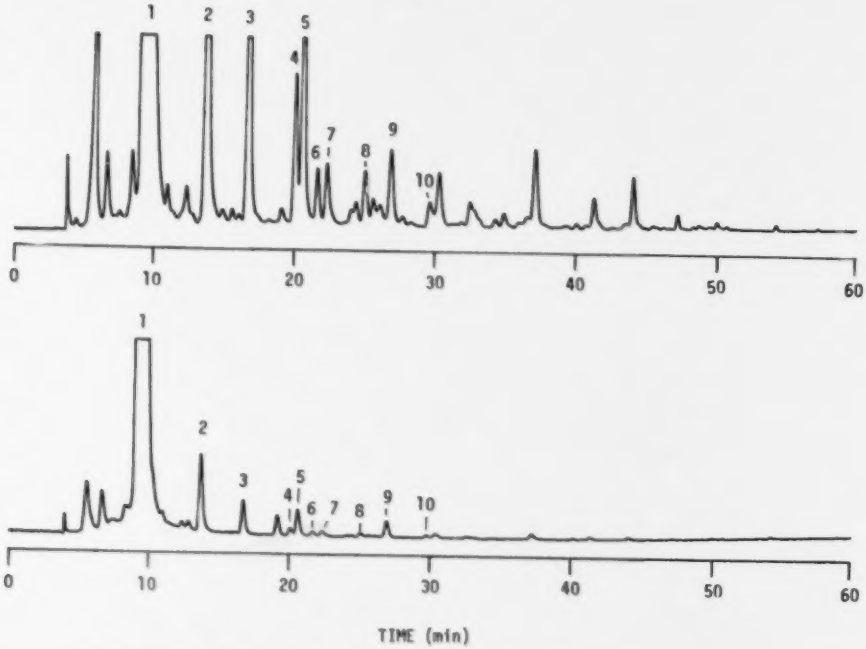

FIGURE 2 Comparative carbonyl profiles of impinger (lower chromatogram) and cartridge (upper chromatogram) of an outdoor ambient air from a residential area with a high concentration of woodburning fireplaces. Chromatographic conditions and identities of numbered peaks as in Figure 1.

consequence, the analytes in the cartridge samples can be measured with more precision than in the corresponding parallel impinger samples. For the same volume of air sampled, the final analytical solution from the cartridge for HPLC analysis is five times as concentrated as the analytical solution from the impinger sample under our experimental procedures.

Table IV illustrates the comparison of both devices for short term (1 h) and long term (12 h) sampling of ambient air. Good correlation for the major components is obtained between the two techniques. Reproducibility of parallel cartridge samples is excellent.

TABLE IV

Comparison of cartridge and impinger for short-term (1 h) and long-term (12 h) sampling for carbonyls in ambient air.

(a) Laboratory air, sampled for 1 h

	Concentration in ppb			
	Run 1		Run 2	
	Imp	Cart	Imp	Cart
Formaldehyde	2.75	2.52	4.11	3.75
Acetaldehyde	1.17	1.59	2.16	2.26
Acrolein		0.07	0.12	0.13
Acetone	1.80	2.43	2.52	2.66
Propionaldehyde		0.21	0.16	0.08
Butyraldehyde		1.00		0.12
Sample volume, L	171.00	81.00	165.00	74.70

(b) Outdoor ambient air, sampled for 12 h

	Concentration in ppb			
	Imp	Cart 1	Cart 2	Cart 3
Formaldehyde	6.29	7.30	7.23	7.38
Acetaldehyde	3.20	4.08	4.05	4.15
Acrolein	1.01	1.14	1.14	1.10
Acetone	3.06	3.67	3.63	3.72
Propionaldehyde	0.36	0.65	0.61	0.60
Crotonaldehyde	0.14	0.32	0.60	0.44
x-Acrolein	0.07		0.27	0.32
Sample volume, L	275	640	907	698

Table V presents some short term stability studies of ambient air samples from a parking lot. The data set is very limited. However, it demonstrates that a cartridge, if properly packaged, can be sent from a field sampling location to a central laboratory for analysis within about two weeks without compromise of sample integrity. The sample can likewise be stored in a refrigerator for over a month with no significant change in the concentration of the known carbonyls.

TABLE V

Stability of carbonyl compounds from a parking lot ambient air on DNPH-coated Sep-PAK cartridges.

	Concentration in ppb				Mean	Sigma
(a) Stability on transit.						
Sample number	III-3	III-2	III-4	III-1		
Date sampled	5/31/85	5/31/85	5/31/85	5/31/85		
Date analyzed	5/31/85	6/11/85	6/11/85	6/12/85		
Formaldehyde	4.35	4.79	3.58	3.90	4.16	0.52
Acetaldehyde	2.10	2.28	2.02	2.38	2.20	0.16
Acetone	3.76	3.30	3.41	3.78	3.56	0.24
Propionaldehyde	0.20	0.25	0.22	0.32	0.24	0.05
Butyraldehyde	0.91	0.84	0.80	2.65	1.30	0.90
x-Butyraldehyde	1.05	2.82	1.33	1.06	1.56	0.84
x-Valeraldehyde	0.32	0.31	0.28	0.21	0.28	0.05
(b) Stability on cold refrigerator storage.						
Sample number	IV-1	IV-3	IV-4			
Date sampled	6/14/85	6/14/85	6/14/85			
Date analyzed	6/17/85	6/20/85	7/25/85			
Formaldehyde	4.64	3.82	4.27		4.24	0.41
Acetaldehyde	2.66	2.14	2.63		2.48	0.29
Acetone	2.95	2.57	2.84		2.79	0.20
Propionaldehyde	0.31	0.22	0.36		0.30	0.07
Butyraldehyde	4.92	2.80	1.67		3.13	1.65
x-Butyraldehyde	0.62	0.62	0.41		0.55	0.12
x-Valeraldehyde	0.10		0.27		0.18	0.12

Note: Samples III-2 and III-4 were sent to and returned from the west coast by mail. Sample III-1 was kept in a capped polypropylene bottle in a refrigerator.

The initial field evaluation of the cartridge for sampling ambient air was conducted during the winter when the mean temperatures were below or near freezing. The cartridges were used as direct probes and traps. The formaldehyde values for the impingers were consistently higher than the corresponding cartridges, with impinger-to-cartridge ratios ranging from about 1.5 to 4.8 (mean temperature $= -2.8°$ to 5°C). The highest value corresponded to a sampling episode with the lowest mean temperature. As a result of these initial observations, subsequent samplings with the cartridges were per-

formed with a heated (~100°C) glass probe similar to that used for impinger sampling. We recommend the use of a heated probe when the ambient temperature is below 10°C.

CONCLUSIONS

Qualitative and quantitative experimental data presented in this paper showed that the DNPH-coated Sep-PAK cartridge and the DNPH/ACN impinger methods are equivalent techniques for sampling carbonyl compounds in ambient air. Significantly higher analytical sensitivity is attainable with the cartridge method due to high degree of preconcentration of the analytes in the HPLC analytical samples. The cartridge is ideal for long-term sampling of carbonyls at sub and low ppb levels such as found in ambient air or for short-term sampling of carbonyls at high and low ppm levels such as found in diluted automotive exhaust emissions.

The olefinic aldehydes, acrolein and crotonaldehyde, show loss on the cartridge samples. However, a quantitative correlation has been shown between the disappearance of acrolein in a sample matrix and the growth of an unknown component, *x*-acrolein. The sum of acrolein and *x*-acrolein appears to be invariant with time and could possibly be used to measure the true concentration of acrolein. Crotonaldehyde concentration was too low to notice a similar relationship as observed for acrolein.

The cartridge is more convenient than the impinger for field applications especially when the samples have to be shipped to a central laboratory for analysis. When properly packed, cartridge samples can be shipped from the field to the laboratory for analysis within two weeks without sacrifice of sample integrity. Samples may be stored in a refrigerator for a month without significant deterioration.

This report has been reviewed by the Atmospheric Sciences Research Laboratory, U.S. Environmental Protection Agency, and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the U.S. Environmental Protection Agency nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

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